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Preparation of Cu Nanoclusters within Dendrimer Templates

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Abstract

A new template synthesis strategy for preparing Cu nanoclusters within dendrimer 'nanoreactors' is demonstrated. Hydroxyl-terminated polyamidoamine (PAMAM) dendrimers of generation higher than 2 act as monodispersed templates as well as stablizers for nanocluster synthesis. Cu^{2+} ions are first quantitatively sorbed into the dendrimer via a strong coordinative interaction with interior amines and then chemically reduced to yield Cu nanoclusters. The nanoclusters are composed of a well-defined number of atoms. Importantly, cluster size can be controlled by varying the size of the host dendrimer nanoreactor (16-atom Cu cluster in G4 and 64-atom Cu cluster in G6 dendrimers). The clusters remain trapped within the dendrimers for extended periods of time, do not agglomerate, and do not precipitate. The clusters can also be oxidized to yield dendrimer-encapsulated Cu^{2+}.

Here we introduce a new template-synthesis strategy for preparing metal nanoclusters within dendrimer 'nanoreactors'. Proof of concept is demonstrated by preparation of Cu clusters because analysis is simplified, but the approach is suitable for most metals. Clusters ranging in size from 4-64 atoms are prepared by irreversible partioning of Cu^{2+} into the interior of a poly(amidoamine) (PAMAM) Starburst™ dendrimers and subsequent chemical reduction (Scheme 1). By controlling the chemical structure and size of the dendrimers, a range of different-size clusters can be prepared.

Small clusters of metals[1] and semiconductors[2] are interesting because of their unique mechanical, electronic, optical, magnetic, and chemical properties. Of particular interest are transition-metal nanoclusters, which are useful for applications in catalysis and electrocatalysis.[3-7] The per-atom catalytic efficiency of metal clusters and colloids often increases as the cluster size decreases. There are at least two reasons for this: (1) the surface-area-to-volume ratio of the metal is enhanced; (2) electronic and structural changes, which are poorly understood at present, occur as particle sizes decrease. Unfortunately, as a consequence of the presence of many unsatisfied metal bonds, the probability of cluster aggregation also increases with decreasing size. The extent of agglomeration can be effectively reduced by lowering the surface energy by adsorption of stabilizers such as polymers or surfactants. However, in effect this corresponds to

poisoning the cluster surface,[8-11] thereby marginalizing

applications such as catalysis. A significant challege,

therefore, is the development of methods for eliminating

aggregation without reducing catalytic efficiency. Another key

challenge involves controlling cluster size and size distribution.

There are two methods in common use for achieving this goal: (1)

optimization of the synthesis conditions for cluster nucleation,

growth, and growth termination; (2) growth of particles within

monodispersed templates such as reversed micelles or porous

membranes.[12-16] By using dendrimers as monodispersed templates for

cluster growth, we achieve both cluster stability and full control

over size and size distrubution, while simultaneously allowing

access of substrates to the cluster surface.[17]

Figure 1a shows absorption spectra of Cu^{2+} coordinated to

different ligands. In the absence of dendrimer, Cu^{2+} exists

primarily as $[Cu(H_2O)_6]^{2+}$, which results in a broad, weak absorption

band centered at 810 nm. This corresponds to the well-known d-d

transition for Cu^{2+} in a tetragonally distorted octahedral or

square-planar ligand field.[18,19] In the presence of hydroxyl-

terminated, fourth generation (G4) PAMAM dendrimers having an

ethylenediamine core (G4-OH), λ_{max} for the d-d transition shifts to

605 nm ($\varepsilon \sim 100$ M^{-1} cm^{-1}, based on the equivalents of Cu^{2+} present).

In addition, a strong band centered at 300 nm ($\varepsilon \sim 4,000$ M^{-1} cm^{-1})

emerges, which can be assigned to the ligand-to-metal-charge-

transfer (LMCT) transition.[20-22]

Figure 1

To learn more about the Cu^{2+} ligand field, we quantitatively assessed the number of Cu^{2+} ions extracted into each dendrimer by spectrophotometric titration (Figure 1b). The data indicate that each G4-OH dendrimer sorbs 16 Cu^{2+} ions. It is tempting to conclude that each Cu^{2+} ion is coordinated with about 4 amine groups since a G4-OH dendrimer contains 62 interior tertiary amines. However, we think it more likely that most of the ions bind to the outermost 16 pairs of tertiary amine groups because models indicate that the dendrimer structure is not well configured for complexation between the inner amines and Cu^{2+}. Thus, on average, each Cu^{2+} is coordinated to two amine groups, and the remaining positions of the ligand field are likely occupied by weakly binding ligands such as amide groups or water molecules.[23,24] This model is fully consistent with the results of spectrophotometric titrations of G2-OH and G6-OH, which contain 4 and 64 pairs of tertiary amines in the outermost shell, and which sorb 4 and 64 Cu^{2+} ions, respectively (Figure 1b inset). In addition, the EPR spectrum of Cu^{2+} coordinated within G4-OH yields a $g_{//}$ factor of 2.22 and a hyperfine coupling constant, $A_{//}$, of 189 cm^{-1} (see supporting material). These values are consistent with the presence of Cu^{2+} in a tetragonal ligand field consisting of 2 amines and 2 other nitrogen- or oxygen-containing ligands.[24-27]

The binding between Cu^{2+} and dendrimer is quite strong and we characterize it here as irreversible: the d-d transition band at 605 nm does not decrease significantly even after 36 h of dialysis against pure water. However, H^+ effectively competes with Cu^{2+} for the tertiary amine sites,[28] and so it is possible to release Cu^{2+} from the G4-OH interior in a pH 1.3 HCl solution.

Chemical reduction of Cu^{2+}-loaded G4-OH dendrimers (G4-OH/Cu^{2+}) with excess $NaBH_4$ results in intradendrimer Cu clusters (Scheme 1). Evidence for this comes from the immediate change in solution color from blue to golden brown: the absorbance bands originally present at 605 nm and 300 nm disappear and are replaced with a monotonically increasing spectrum of nearly exponential slope towards shorter wavelengths (Figure 2). This behavior results from the disappearance of Cu^{2+} and the appearance of a new interband transition arising from the intradendrimer Cu clusters. The measured onset of this transitions at 590 nm agrees with the reported value,[29] and the exponential shape is characteristic of a band-like electronic structure, which strongly suggests that the reduced Cu does not exist as isolated atoms, but rather as clusters.[30] This view is also supported by loss of signal in the EPR spectrum.[31]

Scheme 1

Figure 2

The absence of an absorption peak arising from Mie plasmon resonance (around 570 nm)[32] also indicates that the Cu cluster is smaller than the Mie-onset particle diameter of about 5 nm.[32,33] The plasmon resonance peak cannot be detected for very small metal clusters because the peak is flattened due to the large imaginary dielectric constant for small metal clusters.[30]

Transmission electron microscopy (TEM) results also indicate the presence of intradendrimer Cu clusters after reduction. Micrographs of Cu clusters within G4-OH reveal particles having a diameter less than 2 nm,[34] much smaller than the 4.5 nm diameter of G4-OH.[35,36]

Finally, the intradendrimer Cu clusters are extremely stable despite their small size, which provides additional strong evidence that the clusters reside in the dendrimer interior. Clusters formed in the presence of G4-OH or G6-OH dendrimers and with a Cu^{2+} loading less than the maximum threshold values (Figure 1b) were found to be stable (no observable agglomeration or precipitation) for at least one week in an oxygen-free solution. However, in air-saturated solutions the clusters revert to intradendrimer Cu^{2+} ions overnight. In contrast, when excess Cu^{2+} is added to a dendrimer solution, Cu^{2+} is present both inside the dendrimer and as hydrated ions in solution. After reduction, the excess Cu^{2+} forms a dark precipitate within a few hours, but the remaining transparent solution yields the same absorption spectrum as one prepared with a stoichiometric amount of Cu^{2+}. TEM images of the particles in these solutions reveal two size regimes: the

first is 9 ± 4 nm in average diameter and is responsible for the dark precipitate; the second, which is 1.8 ± 0.3 nm in diameter,[34] corresponds to the intradendrimer cluster.

The ability to prepare well-defined intradendrimer metal nanoclusters depends strongly on the chemical composition of the dendrimer. Spectroscopic results such as those shown in Figure 1 indicate that when amine-terminated G4 PAMAM dendrimers (G4-NH$_2$) are used as templates, they sorb a maximum of 36 Cu^{2+} ions which bind primarily to the terminal primary amine groups. Reduction of a solution containing 0.6 mM Cu^{2+} and 0.05 mM G4-NH$_2$ results in a clearly observable plasmon resonance band at 570 nm (Figure 2),[30,32,33] which indicates that the Cu clusters prepared in this way are > 5 nm in diameter. This larger size is a consequence of agglomeration of Cu particles adsorbed to the unprotected dendrimer exterior.[28,37]

In conclusion, using dendrimers as a synthetic template and as a cluster stabilizer, we have developed a new method for preparing stable metal nanoclusters composed of a well-defined number of atoms. Importantly, cluster size can be controlled by varying the size of the host-dendrimer nanoreactor. At present we believe that some fraction of the cluster surface is not coordinated to internal dendrimer branches, which make these materials uniquely suited for catalysis. Experiments are underway to prove this and better characterize these fascinating new nanocomposite materials.

Acknowledgment

Supporting Information Available

Absorption spectra of solutions of 3.0 mM Cu^{2+} and 0.05 mM Gn-OH (n = 2, 4 and 6) and spectrophotometric titration plots of G4-NH_2 and G4-OH with Cu^{2+} ions; pH effect on the absorbance of solutions of 0.6 mM Cu^{2+} and 0.05 mM G4-OH, 1.5 mM Cu^{2+} and 0.05 mM G4-NH_2; EPR spectra (T = 140 K) of solutions of 0.6 mM Cu^{2+} and 0.05 mM G4-OH before and after reduction (3 pages). See any current masthead page for ordering and Internet access instructions.

Figure captions
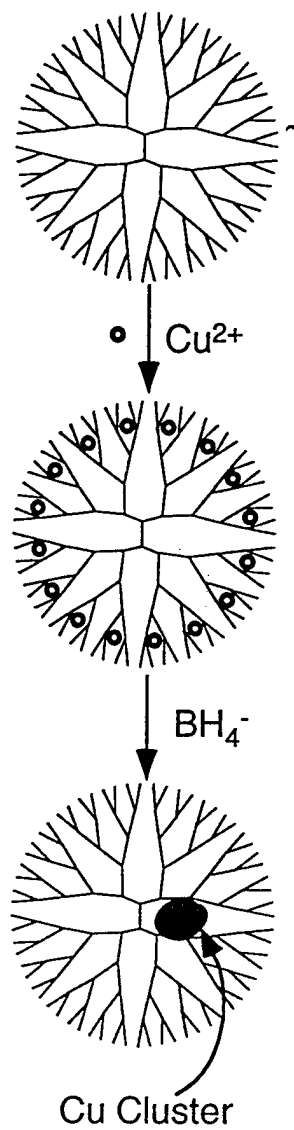
Figure 1. (a) Absorption spectra of 0.6 mM $CuSO_4$ in the presence (solid line, curve 3) and in the absence (dashed line, curve 2) of 0.05 mM G4-OH. Curve 1 is the absorption spectrum of 0.05 mM G4-OH vs. water. (b) Spectrophotometric titration plot: absorbance at the peak maximum of 605 nm as a function of number of Cu^{2+} ions per G4-OH. The initial concentration of G4-OH was 0.05 mM. The inset shows the relationship between the number of Cu^{2+} ions complexed within Gn-OH and the number of 3° amine groups within Gn-OH. All measurements were made with an optical path length of 1 cm.

Figure 2. Absorption spectra of 0.6 mM $CuSO_4$ and 0.05 mM G4-OH before (dashed line, curve 1) and after (solid line, curve 2) reduction with excess amount of $NaBH_4$. Curve 3 was obtained under the same conditions as those for curve 2 except 0.05-mM $G4-NH_2$ was used in place of G4-OH.

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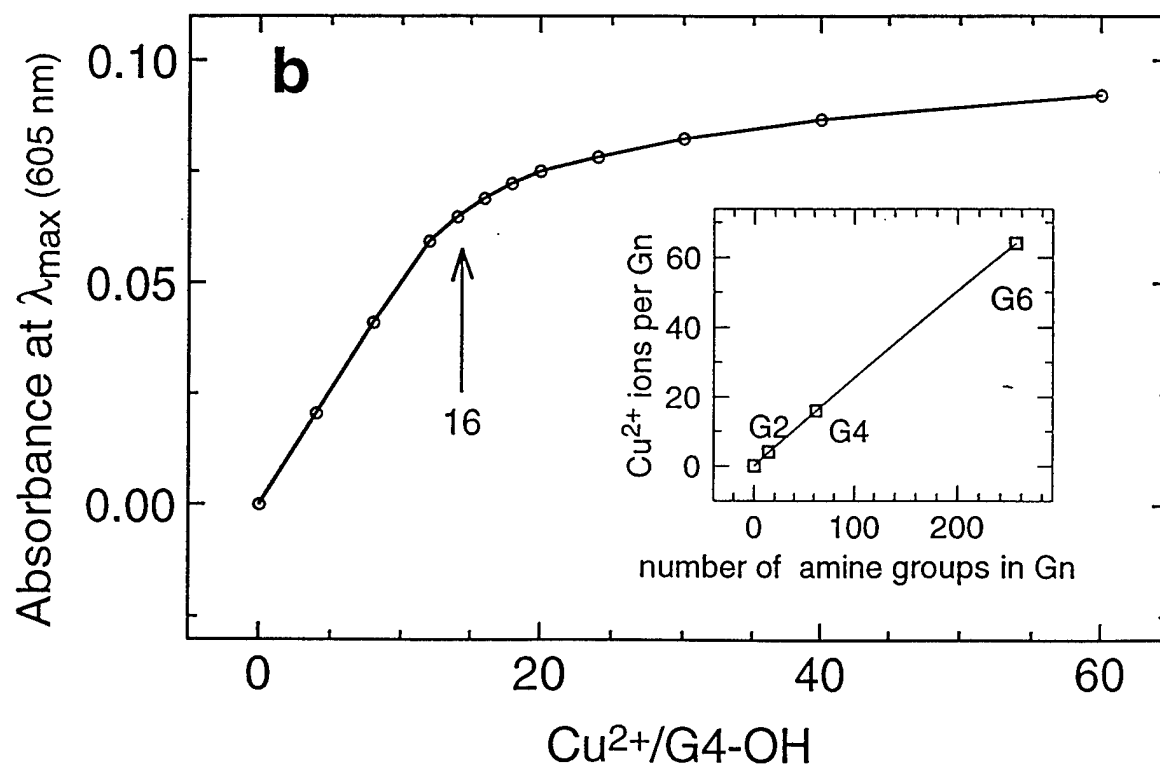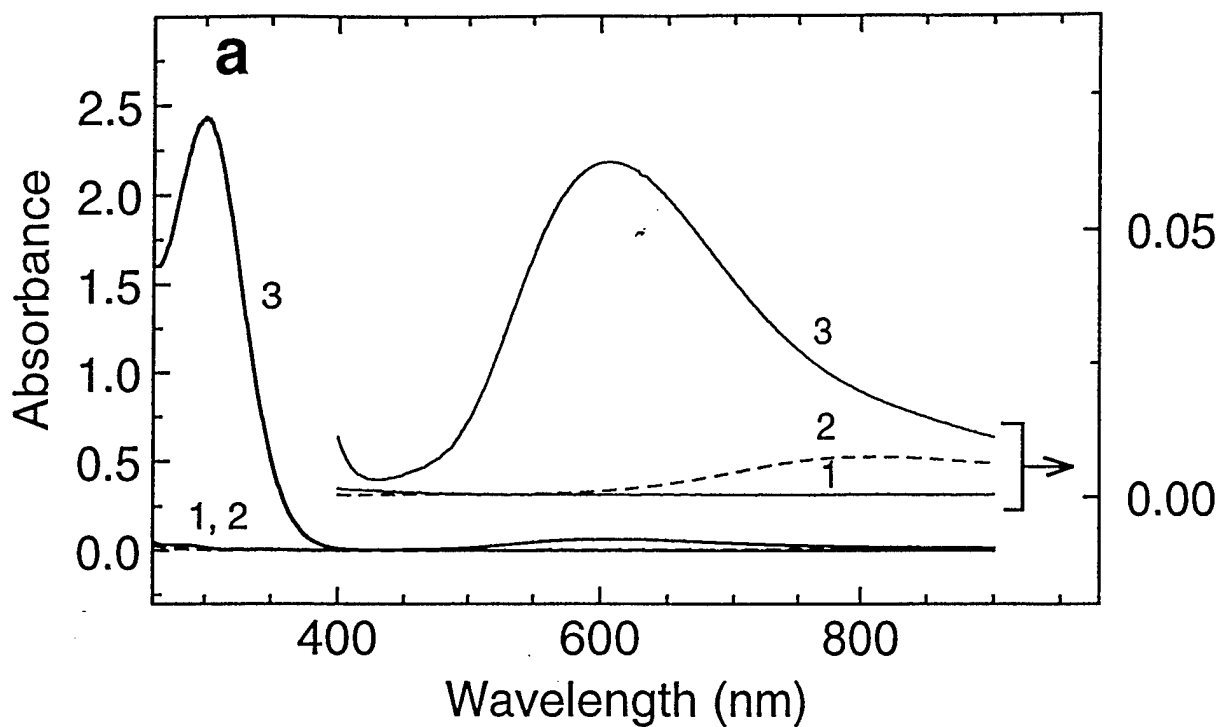
Cu^{2+}

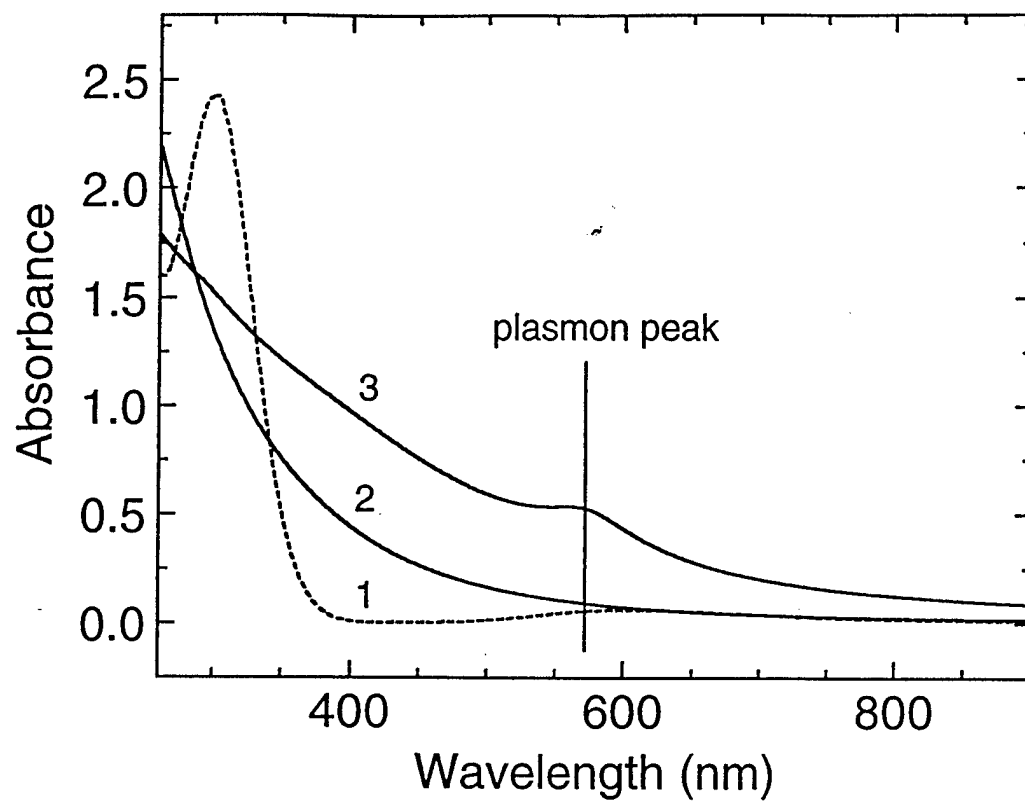BH_4^-

Cu Cluster

Scheme I/Zhao et al.

Figure1/Zhao et al.

Figure 2/Zhao et al.

Supporting Information

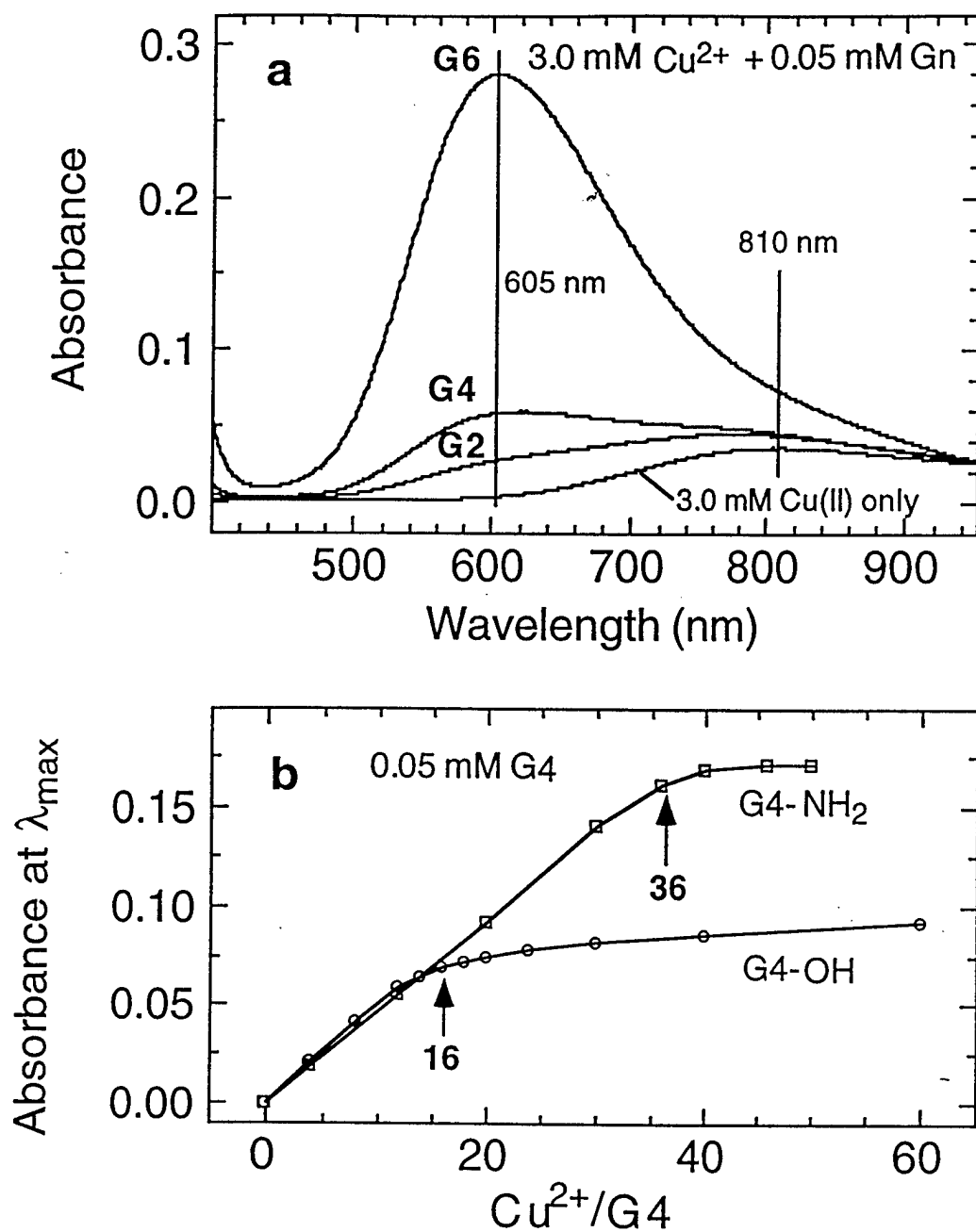# Preparation of Cu Nanoclusters within Dendrimer Templates

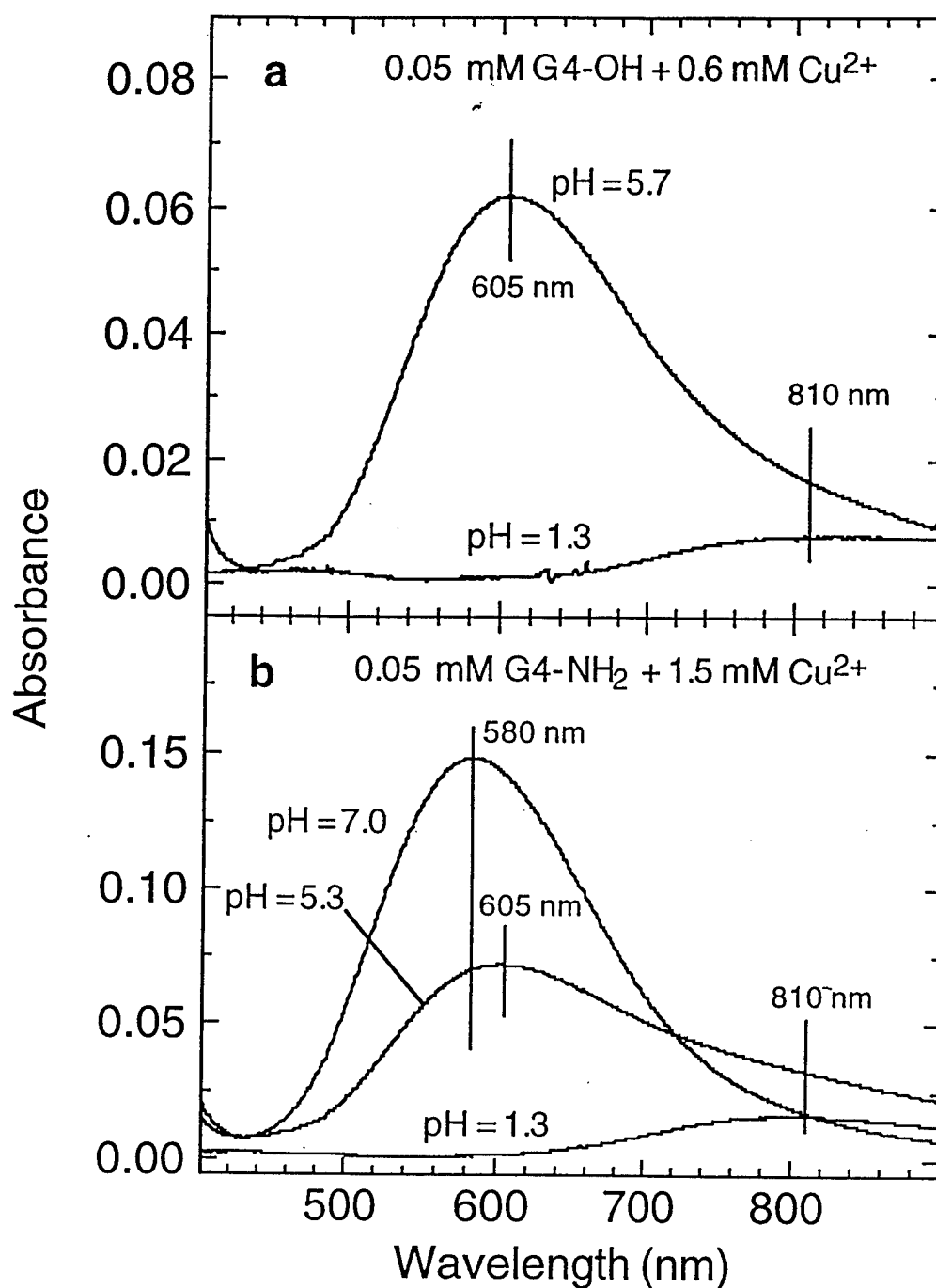Mingqi Zhao, Li Sun, and Richard M. Crooks[*]

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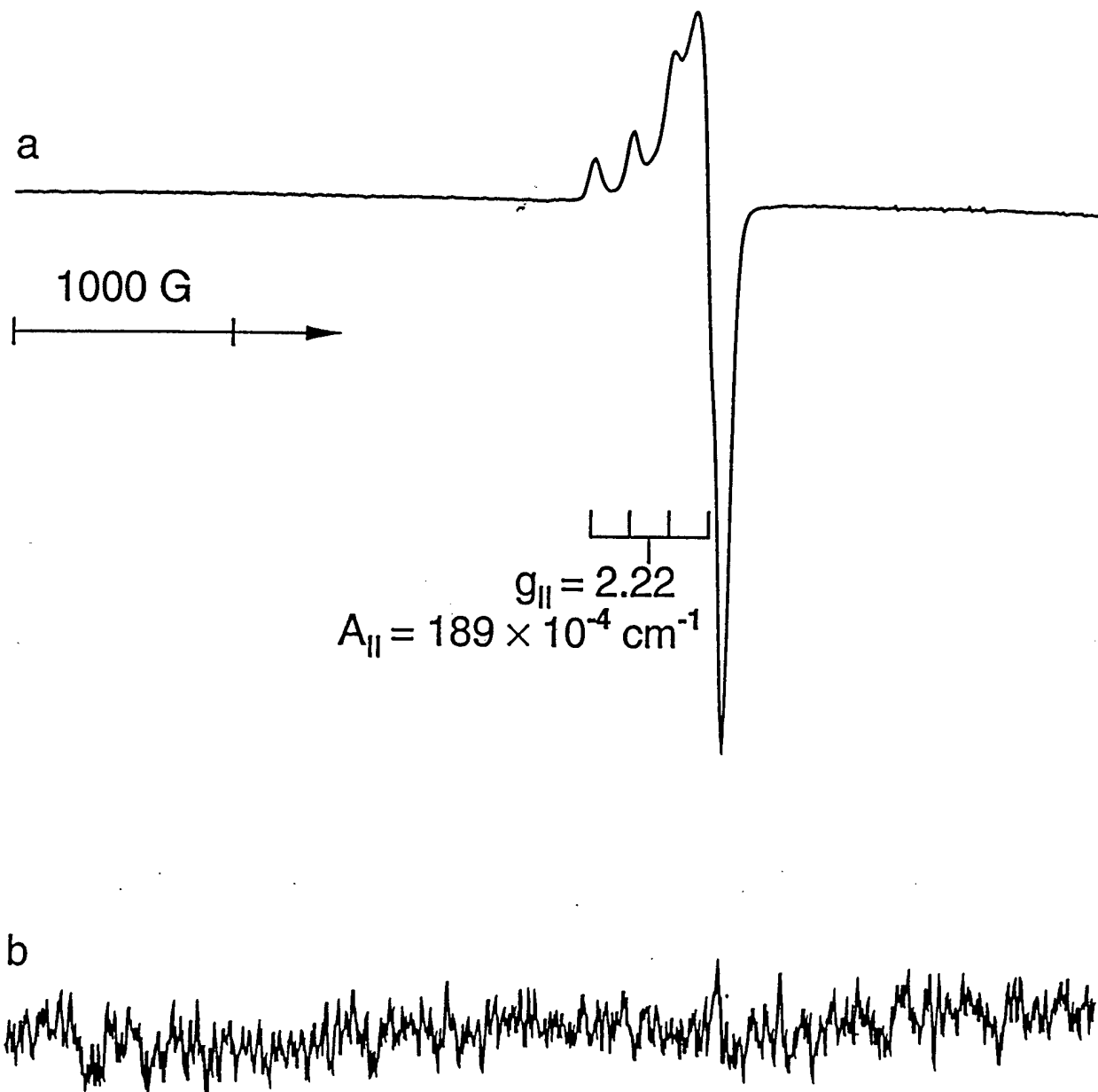
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a. The effect of dendrimer size on the absorbance of 3.0 mM Cu(II) + 0.05 mM Gn-OH. As indicated by the increase in the band at 605 nm, the extent of complexation increases with increasing dendrimer generation.

b. The effect of dendrimer terminal group on the titration curves for G4 PAMAM dendrimers. G4-NH2 complexes 20 more Cu^{2+} ions per dendrimer than G4-OH as a consequence of primary amine interactions with Cu^{2+}.

Figure 1s/Zhao et al.

pH effect on the absorbance of (a) 0.6 mM Cu^{2+} + 0.05 mM G4-OH and (b) 1.5 mM Cu^{2+} + 0.05 mM G4-NH_2. When the pH of solution (a) is adjusted from 5.7 to 1.3 with HCl, no absorption band at 605 nm is observed. When the pH of solution (b) is adjusted from 7.0 to 5.3 with CH_3COOH, we observed a red shift of the absorption band from 580 nm to 605 nm and an increase of the absorbance at 810 nm . Further acidification with HCl results in complete loss of the peak at 605 nm. The loss in peak intensity in all cases is due to protonation of tertiary or primary amines and resulting decomplexation of Cu^{2+} from the dendrimer. The increase in absorbance at 810 nm with decreasing pH arises from hydrated Cu^{2+}. Optical path length = 1 cm.

a

1000 G

$g_{||} = 2.22$
$A_{||} = 189 \times 10^{-4} \ cm^{-1}$

b

EPR spectra (T = 140 K) of solutions of 0.6 mM Cu^{2+} and 0.05 mM G4-OH (a) before and (b) after reduction at. Before reduction, the $g_{//}$ and $A_{//}$ values are consistent with Cu^{2+} complexation by 2 amines and 2 other nitrogen- or oxygen-containing ligands. After reduction of Cu^{2+} by BH_4^-, the absence of an EPR signal indicates Cu cluster formation.

Figure 3s/Zhao et al.